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ABSTRACT

Symmetry methods employed in the ab initio polyatomic program HONDO are extended to the analytic computation of the energy Hessian matrix. A "skeleton" Hessian matrix is calculated from the unique blocks of electron repulsion integrals. The true Hessian matrix is generated by projecting the symmetric component out of the skeleton Hessian. The analysis is valid for many wavefunctions, including closed or open-shell restricted and unrestricted Hartree-Fock wavefunctions, multi-configuration Hartree-Fock wavefunctions, and configuration interaction wavefunctions. We also extend the use of translational invariance previously used for energy gradient calculations. To illustrate the method, we compare the computer time required for the two-electron

contribution to the Hessian matrix of eclipsed ethane, using Pople's 6-31G** basis set and D_{3h} symmetry and various subgroups of D_{3h}. Computational times are roughly inversely proportional to the order of the point group.

INTRODUCTION

The direct computation of the first derivative of molecular energy with respect to nuclear coordinates[1] has proven to be a powerful tool for determining stationary points on multidimensional potential energy surfaces.[2,3] The initial development for a single-configuration Hartree-Fock (HF) wavefunction[4,5,6] has gradually been extended to fully variational correlated wavefunction of the generalized valence bond type,[7,8] to multiconfiguration Hartree-Fock (MCHF) wavefunction,[9] and also to configuration interaction (CI) wavefunctions.[9,10,11]

Formulas for the second derivatives of the energy have been known for some time,[12,13] but have not received much attention, mainly because of the difficulty involved with the calculation of second derivatives of electron repulsion integrals. Instead, vibrational force constants are determined by taking numerical derivatives of the analytically computed components of the gradient.[5,14,15] If the molecule contains N nuclei, then the numerical derivative approach requires 3N+1 or 6N gradient evaluations, depending on whether the numerical derivative is calculated using a one-point or two-point differencing formula. Each gradient calculation corresponds to an atom moved in the x,y,z directions by a small displacement. In addition to the N dependence of the force constant calculation, it is worth noting that a molecule with point-group symmetry loses its symmetry as soon as one atom has been displaced. It is no longer possible to take advantage of symmetry in the calculation of the energy and energy gradient through efficient computational methods.[6,16] Note that for a symmetric molecule it is not necessary to displace all the equivalent atoms. For example, the

force field for the ethane molecule can be calculated with as few as 7 gradient evaluations, instead of 25, because of the equivalencies among carbon and hydrogen atoms. Such an approach has been implemented in the HONDO program available from the NRCC.[17]

The recently developed numerical quadrature based on the Rys polynomial[18,19] for the calculation of electron repulsion integrals has made it possible to compute efficiently the integrals needed for the first and second energy derivatives. The first efficient computation of the energy second derivatives was reported by Pople et al.[20] for closed-shell and unrestricted HF wavefunctions. Recently we have extended the formalism to MCHF and CI wavefunctions. In this approach the full force field of the molecule is obtained in a single calculation, at the equilibrium geometry for example. The force field evaluation no larger has an explicit dependence on the number of atoms. Furthermore for molecules with point group symmetry, it is possible to exploit the symmetry to reduce the computational work.

In this paper we will describe an extension of the method previously used in energy and gradient calculations to take advantage of molecular symmetry. The method is valid for HF, MCHF, and CI wavefunctions of nondegenerate states. In section I we present the working formulas derived in Ref. 9. In section II we define the nomenclature, closely following the notation of Ref. 6. In section III we present the formalism for taking advantage of symmetry, focusing on the electron repulsion contribution to the second derivatives. Section IV presents an extension of the translational invariance property to the calculation of integral second derivatives. In section V we describe briefly

the computer code organization and present some results showing the reduction of computer time with molecular symmetry.

I. ENERGY DERIVATIVES FOR CI WAVEFUNCTIONS

In the CI method we write the n-electron wavefunction as a linear combination of configuration state functions (CSF). Each CSF is a linear combination of Slater determinants built from an orthonormal set of one-particle spin orbitals. In the expansion regime (LCAO), the spin orbitals are written as linear combinations of one-particle atomic basis functions. We represent the ground and excited states of the molecule by

$$\underset{\sim}{\Psi} = \{\Psi_1, \Psi_2, \ldots \Psi_M\} , \tag{I-1}$$

the set of CSF's by

$$\underset{\sim}{\Phi} = \{\Phi_1, \Phi_2, \ldots \Phi_M\} , \tag{I-2}$$

the set of spin orbitals by

$$\underset{\sim}{\phi} = \{\phi_1, \phi_2, \ldots \phi_N\} , \tag{I-3}$$

and the set of atomic basis functions by

$$\underset{\sim}{\chi} = \{\chi_1, \chi_2, \ldots \chi_N\} . \tag{I-4}$$

The molecular energy is the expectation value of the nonrelativistic electronic Hamiltonian of the molecule. The latter may be written:

$$\mathcal{H} = -\frac{1}{2} \sum_{\mu=1}^{n} \nabla_\mu^2 + \sum_{\mu=1}^{n} v_\mu + \sum_{\mu>\nu}^{n} r_{\mu\nu}^{-1} + V_{\text{nuclear}}, \tag{I-5}$$

where $-\frac{1}{2}\nabla_\mu^2$ is the kinetic energy operator of electron μ, v_μ is the potential experienced by electron μ in the field of all the nuclei, $r_{\mu\nu}^{-1}$ is the Coulomb electron repulsion operator between μ and ν, and $V_{nuclear}$ is the nuclear repulsion operator.

Let $\underset{\sim}{\mathbb{C}}$ be the matrix of coefficients of the ground and excited states of the molecule in the $\underset{\sim}{\Phi}$ basis:

$$\underset{\sim}{\Psi} = \underset{\sim}{\Phi}\ \underset{\sim}{\mathbb{C}} \ . \tag{I-6}$$

Let $\mathbb{E}$ be the diagonal matrix of the energies, and $\mathbb{H}$ the CI matrix. We have

$$\underset{\sim}{\mathbb{H}}\,\underset{\sim}{\mathbb{C}} = \underset{\sim}{\mathbb{C}}\ \underset{\sim}{\mathbb{E}} \ , \tag{I-7}$$

with

$$\underset{\sim}{\mathbb{C}}^{+}\underset{\sim}{\mathbb{C}} = \underset{\sim}{\mathbb{1}} \ . \tag{I-8}$$

Furthermore let $\underset{\sim}{C}$ denote the expansion matrix of the spin orbitals $\underset{\sim}{\phi}$ in the atomic basis $\underset{\sim}{\chi}$:

$$\underset{\sim}{\phi} = \underset{\sim}{\chi}\underset{\sim}{C} \ . \tag{I-9}$$

For the P^{th} molecular state, the energy gradient is given by

$$d\mathbb{E}_P = \underset{\sim}{\mathbb{C}}_P^{+}\ d\underset{\sim}{\mathbb{H}}\ \underset{\sim}{\mathbb{C}}_P \tag{I-10}$$

and the energy second derivative by

$$d^2\mathbb{E}_P = \underset{\sim}{\mathbb{C}}_P^{+}\ d^2\underset{\sim}{\mathbb{H}}\ \underset{\sim}{\mathbb{C}}_P - 2\sum_{P\neq Q}\frac{\left|\underset{\sim}{\mathbb{C}}_P^{+}\ d\underset{\sim}{\mathbb{H}}\ \underset{\sim}{\mathbb{C}}_Q\right|^2}{\mathbb{E}_Q - \mathbb{E}_P} \ . \tag{I-11}$$

Alternatively

$$d^2\mathbb{E}_p = \underset{\sim}{\mathbb{C}}_p^+ \, d^2\underset{\sim}{\mathbb{H}} \, \underset{\sim}{\mathbb{C}}_p + 2 \, \underset{\sim}{\mathbb{C}}_p^+ \, [d\underset{\sim}{\mathbb{H}} - d\mathbb{E}_p \, \underset{\sim}{\mathbb{1}}] \, d\underset{\sim}{\mathbb{C}}_p \, , \qquad \text{(I-12)}$$

where $d\underset{\sim}{\mathbb{C}}_p$ is the solution of the inhomogeneous system of coupled equations:

$$[\underset{\sim}{\mathbb{H}} - \mathbb{E}_p \, \underset{\sim}{\mathbb{1}}] \, d\underset{\sim}{\mathbb{C}}_p = - \, [d\underset{\sim}{\mathbb{H}} - d\mathbb{E}_p \, \underset{\sim}{\mathbb{1}}] \, \underset{\sim}{\mathbb{C}}_p \, . \qquad \text{(I-13)}$$

The total energy and the CI matrix elements can be written under the general form

$$\mathbb{H} = \sum_{i,j}^{occ} \gamma^{ij} \, \langle i|h|j\rangle + \frac{1}{2} \sum_{ijk\ell}^{occ} \Gamma^{ijk\ell} \, \langle ij|r_{12}^{-1}|k\ell\rangle \, , \qquad \text{(I-14)}$$

where γ^{ij} and $\Gamma^{ijk\ell}$ are the one- and two-particle density elements, h is the usual one-electron bare nucleus operator, and "occ" represents the set of occupied molecular orbitals. It follows that

$$\begin{aligned} d\mathbb{H} \; = & \sum_{i,j}^{occ} \sum_{\mu,\nu}^{N} \gamma^{ij} \, C_{\mu i} \, C_{\nu j} \, d(\mu|h|\nu) \\ & + \frac{1}{2} \sum_{ijk\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell} \, C_{\mu i} \, C_{\nu j} \, C_{\rho k} \, C_{\sigma \ell} \, d(\mu\nu|r_{12}^{-1}|\rho\sigma) \qquad \text{(I-15)} \\ & + 2 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri} \, \varepsilon^{ri} \end{aligned}$$

and

$$
\begin{aligned}
d^2\mathbb{H} = & \sum_{i,j}^{occ} \sum_{\mu\nu}^{N} \gamma^{ij}\, C_{\mu i}\, C_{\nu j}\, d^2(\mu|h|\nu) \\
& + \frac{1}{2} \sum_{ijk\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell}\, C_{\mu i}\, C_{\nu j}\, C_{\rho k}\, C_{\sigma \ell}\, d^2(\mu\nu|r_{12}^{-1}|\rho\sigma \\
& + 4 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri}\, d\varepsilon^{ri} \\
& + 2 \sum_{i}^{occ} \sum_{r}^{N} d^2U_{ri}\, \varepsilon^{ri} \\
& + 2 \sum_{i,k}^{occ} \sum_{r,s}^{N} dU_{ri} \left[\langle r|F^{ik}|s\rangle + 2 \sum_{j,\rho} \Gamma^{ijk\ell} \langle rj|r_{12}^{-1}|s\ell\rangle \right] dU_{sk} \,,
\end{aligned}
\tag{I-16}
$$

with

$$
\langle r|F^{ij}|s\rangle = \gamma^{ij} \langle r|h|s\rangle + \sum_{k\ell}^{occ} \Gamma^{ijk\ell} \langle rs|r_{12}^{-1}|k\ell\rangle \,, \tag{I-17}
$$

$$
\varepsilon^{ri} = \sum_{j}^{occ} \sum_{\mu\nu}^{N} \gamma^{ij}\, C_{\mu r} C_{\nu j}\, (\mu|k|\nu) + \sum_{jk\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk} C_{\mu r} C_{\nu j} C_{\rho k} C_{\sigma \ell}\, (\mu\nu|r_{12}^{-1}|\rho\sigma), \tag{I-18}
$$

$$
d\varepsilon^{ri} = \sum_{j}^{occ} \sum_{\mu\nu}^{N} \gamma^{ij} C_{\mu r}\, C_{\nu j}\, d(\mu|h|\nu) + \sum_{j,k,\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell}\, C_{\mu r} C_{\nu j} C_{\rho k} C_{\sigma \ell}\, d(\mu\nu|r_{12}^{-1}|\rho\sigma). \tag{I-19}
$$

In Eqs. (I-15) and (I-16) $d\underset{\sim}{U}$ and $d^2\underset{\sim}{U}$ are the first and second derivatives of the molecular orbital coefficients. They are obtained by the Coupled Perturbed Multiconfiguration Hartree-Fock theory.[9,21,22] Note that for a fully variational wavefunction, HF or MCHF, $d\underset{\sim}{U}$ is not required for the gradient calculation, only for the second derivative calculation.

Indeed, it can be shown[9] that

$$2 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri} \, \varepsilon^{ri} = - \sum_{i,r}^{occ} \sum_{\mu\nu}^{N} \varepsilon^{ri} C_{\mu i} C_{\nu r} \, d(\mu|\nu) \ , \qquad \text{(I-20)}$$

and

$$\begin{aligned} 2 \sum_{i}^{occ} \sum_{r}^{N} d^2U_{ri} \, \varepsilon^{ri} = & - \sum_{i,r}^{occ} \sum_{\mu\nu}^{N} \varepsilon^{ri} \, C_{\mu i} \, C_{\nu r} \, d^2(\mu|\nu) \\ & - 2 \sum_{i,r}^{occ} \Bigg\{ 2 \sum_{s}^{N} \sum_{\mu\nu}^{N} \varepsilon^{ri} dU_{si} \, C_{\mu s} \, C_{\nu r} \, d(\mu|\nu) \\ & + \sum_{s}^{N} \varepsilon^{ri} \, dU_{si} \, dU_{sr} \Bigg\} \ . \qquad \text{(I-21)} \end{aligned}$$

In Ref. 6, we have shown how point group symmetry can be used to reduce the computational labor in the electron repulsion contribution of Eq. (I-15). In what follows, we will extend the analysis to the electron repulsion contribution of Eq. (I-16).

II BASIS FUNCTIONS AND SYMMETRY TRANSFORMATIONS

Let χ be a real Cartesian basis function:

$$\chi(Q,n_x,n_y,n_z;r) = (x-Q_x)^{n_x}\,(y-Q_y)^{n_y}\,(z-Q_z)^{n_z}\,g(|r-Q|)\ , \quad \text{(II-1)}$$

where n_x, n_y, n_z are non-negative integers, $\underset{\sim}{Q}$ is the nuclear center of the function, and $\underset{\sim}{r}$ the argument of the function. We introduce the "rotational quantum number"

$$\lambda = n_x + n_y + n_z \quad \text{(II-2)}$$

and refer to a function as being of type s,p,d, etc. when λ equals 0,1,2, respectively. In what follows, we may drop unimportant indices when it is felt that the meaning is obvious from the context.

Let χ^h and χ^{hg} denote the first and second derivatives of χ with respect to Q_x, Q_y, and Q_z when h and g each equal 1, 2, or 3 respectively. Basis functions are grouped into shells. Functions in the same shell have the same Q and λ, so an alternative notation is

$$\chi(I,m) = \chi(\underset{\sim}{Q}_I,\ n_x,\ n_y,\ n_z;\ r)\ . \quad \text{(II-3)}$$

Let G be the point group of the molecule, and R an element of G. Operator $\hat{R}$ maps point $\underset{\sim}{r}$ into $\underset{\sim}{r}'$, function $f(\underset{\sim}{r})$ into $f'(\underset{\sim}{r})$ and shell I into I'. Shells I and I' have the same λ and their centers are related by

$$Q_{I'} = \hat{R}Q_I\ . \quad \text{(II-4)}$$

Basis function $\chi(I,m)$ maps into a linear combination of functions in shell I' that is given by

$$\hat{R}\,\chi(I,m) = \sum_{m'=1}^{M(\lambda)} \chi(I',m')\; R(\lambda_I;\, m', m) \qquad \text{(II-5)}$$

where $M(\lambda) = (\lambda+1)(\lambda+2)/2$ since we insist that a shell be closed under rotation about its own center, and thus include all combinations (n_x, n_y, n_z) consistent with a given λ_I. In Ref. 6 we showed that the effect of a symmetry operation on a basis function derivative χ^h is given by

$$\hat{R}\chi^h(I,m) = \sum_{m'} \sum_{h'} \chi^{h'}(I',m')\; R(1,h',h)\; R(\lambda,m',m)\;. \qquad \text{(II-6)}$$

Similarly it is easy to show that the effect of $\hat{R}$ on a basis function second derivative χ^{hg} is given by

$$\hat{R}\chi^{hg}(I,m) = \sum_{m'} \sum_{h'} \sum_{g'} \chi^{h'g'}(I',m')\, R(1,h',h)\, R(1,g',g)\, R(\lambda,m',m)\;. \qquad \text{(II-7)}$$

III. SECOND DERIVATIVE OF ELECTRON REPULSION ENERGY

Experience indicates that most of the computational labor in computing gradients goes into the electron repulsion contribution, the second term in (I-15). In general an electron repulsion integral $(\mu\nu|r_{12}^{-1}|\rho\sigma)$ depends on 12 nuclear coordinate parameters, and thus 12 integral derivatives must be calculated. The translational invariance reduces these to only 9 contributions; however, most of the computation time is consumed in calculating $d(\mu\nu|r_{12}^{-1}|\rho\sigma)$. For the second-derivative electron repulsion contribution, the second term in (I-16), an integral will contribute to 78 independent second derivatives. Although these can be reduced to 45 contributions because of translational invariance (see below), it is expected to dominate the calculation of (I-16). Indeed, Pople et al.[20] showed that evaluation of second-derivative integrals requires about twice the time as that for the integral first derivatives.

To simplify the analysis, we consider

$$E = \sum_{\mu\nu\rho\sigma} P_{\mu\nu\rho\sigma} (\mu\nu||\rho\sigma) , \qquad \text{(III-1)}$$

where we use the notation $(\mu\nu||\rho\sigma)$ to represent the integral $\langle \chi_\mu(1)\, \chi_\nu(1)|r_{12}^{-1}|\chi_\rho(2)\, \chi_\sigma(2)\rangle$. Let q_α^h denote the h^{th} coordinate of nucleus α. A contribution to the Hessian matrix is given by

$$E_{\alpha\beta}^{hg} = \sum_{\mu\nu\rho\sigma} P_{\mu\nu\rho\sigma} \frac{\partial^2}{\partial q_\alpha^h \partial q_\beta^g} (\mu\nu||\rho\sigma) . \qquad \text{(III-2)}$$

If μ^h and μ^{hg} denote the derivatives, χ_μ^h and χ_μ^q, then

$$E^{hg}_{\alpha\beta} = \sum_{\mu\nu\rho\sigma} P_{\mu\nu\rho\sigma} \Big[(\mu^{hg}\nu\|\rho\sigma)\,\delta(\alpha,\alpha_\mu)\,\delta(\beta,\alpha_\mu) + (\mu\nu^{hg}\|\rho\sigma)\,\delta(\alpha,\alpha_\nu)\,\delta(\beta,\alpha_\nu)$$

$$+ (\mu\nu\|\rho^{hg}\sigma)\,\delta(\alpha,\alpha_\rho)\,\delta(\beta,\alpha_\rho) + (\mu\nu\|\rho\sigma^{hg})\,\delta(\alpha,\alpha_\sigma)\,\delta(\beta,\alpha_\sigma)$$

$$+ (\mu^{h}\nu^{g}\|\rho\sigma)\,\delta(\alpha,\alpha_\mu)\,\delta(\beta,\alpha_\nu) + (\mu^{h}\nu\|\rho^{g}\sigma)\,\delta(\alpha,\alpha_\mu)\,\delta(\beta,\alpha_\rho) + (\mu^{h}\nu\|\rho\sigma^{g})\,\delta(\alpha,\alpha_\mu)\,\delta(\beta,\alpha_\sigma)$$

$$+ (\mu^{g}\nu^{h}\|\rho\sigma)\,\delta(\beta,\alpha_\mu)\,\delta(\alpha,\alpha_\nu) + (\mu^{g}\nu\|\rho^{g}\sigma)\,\delta(\beta,\alpha_\mu)\,\delta(\alpha,\alpha_\rho) + (\mu^{g}\nu\|\rho\sigma^{h})\,\delta(\beta,\alpha_\mu)\,\delta(\alpha,\alpha_\sigma)$$

$$+ (\mu\nu^{h}\|\rho^{g}\sigma)\,\delta(\alpha,\alpha_\nu)\,\delta(\beta,\alpha_\rho) + (\mu\nu^{h}\|\rho\sigma^{g})\,\delta(\alpha,\alpha_\nu)\,\delta(\beta,\alpha_\sigma)$$

$$+ (\mu\nu^{g}\|\rho^{h}\sigma)\,\delta(\beta,\alpha_\nu)\,\delta(\alpha,\alpha_\rho) + (\mu\nu^{g}\|\rho\sigma^{h})\,\delta(\beta,\alpha_\nu)\,\delta(\alpha,\alpha_\sigma)$$

$$+ (\mu\nu\|\rho^{h}\sigma^{g})\,\delta(\alpha,\alpha_\rho)\,\delta(\beta,\alpha_\sigma)$$

$$+ (\mu\nu\|\rho^{g}\sigma^{h})\,\delta(\beta,\alpha_\rho)\,\delta(\alpha,\alpha_\sigma)\Big] \qquad \text{(III-3)}$$

The Kroneker deltas in (III-3) express the fact that χ_μ on nucleus α_μ is unaffected by displacement of another center α. In shell notation, (III-3) becomes a sum over eight indices: I, J, K, L, m_μ, m_ν, m_ρ, m_σ. Let $\Delta E^{hg}_{\alpha\beta}$ (IJKL) denote the partial sum in (III-2) corresponding to μ, ν, ρ, σ running over the basis functions in shells I, J, K, and L, respectively.

$$\Delta E^{hg}_{\alpha\beta}(\mathrm{IJKL}) = \sum_{m_\mu,m_\nu,m_\rho,m_\sigma} [16\ \text{terms}]\ P(\mathrm{IJKL}, m_\mu, m_\nu, m_\rho, m_\sigma) \qquad \text{(III-4)}$$

If G4 denotes the grande list of the four labels IJKL (see Ref. 16), then

$$\Delta E_{\alpha\beta}^{hg} = \sum_{G4} \Delta E_{\alpha\beta}^{hg} (IJKL) \ . \qquad \text{(III-5)}$$

For each four-label, one computes 78 blocks of integrals, with each block contributing to one and only one element of the Hessian matrix.

As for the gradient, the summation over G4 in (III-5) can be replaced by a sum over P4, the petite list of four labels (see Ref. 16), which includes only the unique four labels. If I'J'K'L' and I"J"K"L" are equivalent under the trivial symmetries (i.e. index permutation), then it is clear that

$$\Delta E_{\alpha\beta}^{hg} (I'J'K'L') = \Delta E_{\alpha\beta}^{hg} (I"J"K"L") \ , \qquad \text{(III-6)}$$

so that it suffices to compare $\Delta E_{\alpha\beta}^{hg}$ (IJKL) with $\Delta E_{\alpha\beta}^{hg}$ (I'J'K'L') when IJKL and I'K'K'L' are equivalent under the point group symmetries. The unitary property of a symmetry transformation leads to

$$(\mu^{hg}\nu \| \rho\sigma) = \langle (\hat{R}\chi_\mu^{hg}) (\hat{R}\chi_\nu) | r_{12}^{-1} | (\hat{R}\chi_\rho) (\hat{R}\chi_\sigma) \rangle \qquad \text{(III-7)}$$

and

$$(\mu^h\nu^g \| \rho\sigma) = \langle (\hat{R}\chi_\mu^h)(\hat{R}\chi_\nu^g) | r_{12}^{-1} | (\hat{R}\chi_\rho) (\hat{R}\chi_\sigma) \rangle \ . \qquad \text{(III-8)}$$

We substitute Eqs. (II-5), (II-6), and (II-7) into Eqs. (III-7) and (III-8), and into Eq. (III-3), and use the following equation:

$$\sum_{m_\mu m_\nu m_\rho m_\sigma} R(\lambda_I, m'_\mu, m_\mu)\, R(\lambda_J, m'_\nu, m_\nu)\, R(\lambda_K, m'_\rho, m_\rho)\, R(\lambda_L, m'_\sigma, m_\sigma)\, P(IJKL, m_\mu, m_\nu, m_\rho, m_\sigma)$$

$$= P(I'J'K'L', m'_\mu, m'_\nu, m'_\rho, m'_\sigma) \ , \qquad \text{(III-9)}$$

valid when the electronic charge density transforms according to the totally symmetric representation of the point group. Equation (III-9) eliminates the unprimed indices, while summation over primed indices gives $\Delta E^{hg}_{\alpha\beta}(I'J'K'L')$. Thus we have obtained the very important result

$$\Delta E^{hg}_{\alpha\beta}(IJKL) = \sum_{h'g'} \Delta E^{h'g'}_{\alpha\beta}(I'K'K'L')\, R(1,h',h)\, R(1,g',g). \qquad \text{(III-10)}$$

Equation (III-10) allows us to eliminate most of the terms in the summation of Eq. (III-5). Let $q_4(IJKL)$ be the number of four labels equivalent to IJKL under the direct product of trivial symmetries and point group symmetries. We change the order of summations in Eqs. (III-5) and (III-10) and define the "skeleton Hessian matrix" as:

$$E^{*hg}_{\alpha\beta} = \sum_{P4} q_4(IJKL)\, \Delta E^{hg}_{\alpha\beta}(IJKL) \ . \qquad \text{(III-11)}$$

From this, the true Hessian matrix is obtained by a final "symmetrization":

$$E^{hg}_{\alpha\beta} = ng^{-1} \sum_R \sum_{h'} \sum_{g'} E^{*h'g'}_{\alpha'\beta'}\, R(1,h',h)\, R(1,g',g) \ , \qquad \text{(III-12)}$$

where ng is the order of the symmetry point group. In other words, the true Hessian matrix is obtained by projecting the completely symmetric component out of the skeleton Hessian matrix.

IV. TRANSLATIONAL INVARIANCE

In the preceding section we have shown how to replace the summation over the grande list G4 in Eq. (III-5) with a summation over the petite list P4. According to Eq. (III-4), each term in Eq. (III-11) is itself a sum of 16 M_{block} contributions, where $M_{block} = M(\lambda_I)\, M(\lambda_J)\, M(\lambda_K)\, M(\lambda_L)$. We identify the 16 terms by two indices, t and u, running from one to four separately. In this section we discuss an additional relationship which allows us to eliminate certain (t,u) values.

For a given IJKL four label, we define sixteen 3x3 matrices $\Delta E(t,u)$ $(t=1,4;\ u=1,4)$. The values $t=1,\ldots 4$ refer to centers $\alpha_I \ldots \alpha_L$ respectively. For example

$$\Delta E(2,3) = \sum_{hg} \sum_{m_\mu m_\nu m_\rho m_\sigma} P(IJKL,m_\mu,m_\nu,m_\rho,m_\sigma)\ \langle \chi(I,m_\mu)\, \chi^h(J,m_\nu) \| \chi^g(K,m_\rho)\, \chi(L,m_\sigma) \rangle \tag{IV-1}$$

As pointed out by Komornicki et al.[4], the translational invariance of an individual integral implies

$$(\mu^h\nu\|\rho\sigma) + (\mu\nu^h\|\rho\sigma) + (\mu\nu\|\rho^h\sigma) + (\mu\nu\|\rho\sigma^h) = 0\ . \tag{IV-2}$$

Further differentiation of Eq. (IV-2) with respect to an arbitrary nuclear coordinate q of the integral gives

$$\frac{\partial}{\partial q}\left((\mu^h\nu\|\rho\sigma) + (\mu\nu^h\|\rho\sigma) + (\mu\nu\|\rho^h\sigma) + (\mu\nu\|\rho\sigma^h)\right) = 0 \tag{IV-3}$$

which leads to

$$\sum_{u=1}^{4} \Delta E(t,u) = 0 \ . \qquad \text{(IV-4)}$$

Anyone of the centers associated with a given IJKL can be eliminated using Eq. (IV-4). Thus only 45 second-derivative integrals out of 78 unique ones need be calculated for a given IJKL Block. Redundancies among the 4 centers lead to an even greater savings.

V. RESULTS

We have implemented these ideas into a new version of HONDO that computes the energy second derivatives for an HF, MCHF or CI wavefunction.

A. Program Organization

After calculation of the molecular wavefunction, the gradient vector and Hessian matrix are computed. The two-electron portion of the Hessian program executes an outer loop over the petite list of four labels. For each unique IJKL the appropriate block of $P_{\mu\nu\rho\sigma}$ is calculated (for an HF wavefunction) or read in (for a MCHF or CI wavefunction) prior to looping over (t,u) labels. For each unique $\Delta E(t,u)$ the program generates three or four intermediate blocks of integrals over shells of contracted Cartesian gaussian functions, and then performs an inner sum over the four m indices. For example, for a DDDD block (λ=2 for all 4 labels) the program calculates a SDDD, DDDD, and GDDD block for $\Delta E(1,1)$, and a PPDD, PFDD, FPDD, and FFDD block for $\Delta E(1,2)$, etc. The $\Delta E(t,u)$ vector is then obtained by summing over m., after combining the integrals from the 3 or 4 blocks to produce the second derivative integrals and multiplying by $P_{\mu\nu\rho\sigma}$. After looping over (t,u), the $\Delta E(t,u)$ matrices are added into the appropriate elements of the skeleton Hessian matrix. After looping over P4 labels, the symmetrization is performed.

B. Computation Times for Ethane

Computations have been carried out for the C_2H_6 molecule in the eclipsed configuration with bond lengths C-C = 1.54068 Å, GH = 1.08622 Å, and angles HCH = 107.05° and CCH = 111.76°, using Pople's 6-31G basis

augmented with a set of d functions on C (α_d = 0.8) and a set of p functions on H (α_p = 0.75). The energy gradient and Hessian matrix were computed using the full D_{3h} symmetry, and the entire calculation repeated using seven different subgroups. The same test calculations were used in Ref. (6). Ratios of computational times are reported in Table I. The effect of using point group symmetry is immediately evident. The results are similar to the one reported for the 2 electron gradient calculation. Not so surprisingly, computation times are roughly inversely proportional to the order of the group.

In conclusion, it is worthwhile comparing the present method of analytical evaluation of the Hessian matrix with the widely used numerical difference method. As shown in Table I, if we take as a unit the time required for the evaluation of the gradient using D_{3h} symmetry, then the direct evaluation of the Hessian will cost 2.4. With the finite difference method, at least 6 gradient evaluations would have to be carried out using C_1 symmetry, in addition to the initial gradient, for a total of 49 units. The direct hessian evaluation is therefore far superior to the finite difference method. The advantage will be even greater with MCHF and CI wavefunctions.

Table 1. Ratio of computation times for eclipsed ethane using 6-31G** basis.

Run	Point Group	Order	2-electron Gradient	2-electron Hessian	Hessian / gradient
1	D_{3h}	12	1	1	2.4
2	C_{3v}	6	1.9	2.0	2.5
3	C_{2v}	4	2.4	2.3	2.3
4	C_3	3	2.8	2.8	2.4
5	C_2	2	4.0	4.0	2.4
6	$Cs(\sigma_h)$	2	4.0	4.0	2.4
7	$Cs(\sigma_v)$	2	4.6	4.9	2.6
8	C_1	1	7.9	7.8	2.4

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